

(12) **UK Patent Application** (19) **GB** (11) **2 357 061** (13) **A**

(43) Date of A Publication 13.06.2001

(21) Application No 0029163.3

(22) Date of Filing 29.11.2000

(30) Priority Data

(31) 99124020 (32) 08.12.1999 (33) EP

(71) Applicant(s)

Merck Patent GmbH
(Incorporated in the Federal Republic of Germany)
Frankfurter Strasse 250, D-64293 Darmstadt,
Federal Republic of Germany

(72) Inventor(s)

David Coates
John Patrick

(74) Agent and/or Address for Service

Venner Shipley & Co
20 Little Britain, LONDON, EC1A 7DH,
United Kingdom

(51) INT CL⁷

B44C 1/17 , B41M 1/24

(52) UK CL (Edition S)

B6J JF2 J804

(56) Documents Cited

EP 0911758 A2

(58) Field of Search

UK CL (Edition S) B6J JE JF2 JF9
INT CL⁷ B41M 1/24 3/12 3/14 , B44C 1/17
Online:EPODOC,WPI,JAPIO

(54) Abstract Title

Hot stamping foils

(57) The invention relates to hot stamping foils comprising at least one layer of liquid crystal material. Such hot stamping foils are used for decorative uses, information storage and security applications. The liquid crystal material comprises polymerized and unpolymerized material. The polymerized material may be a linear or crosslinked liquid crystal side chain polymer.

GB 2 357 061 A

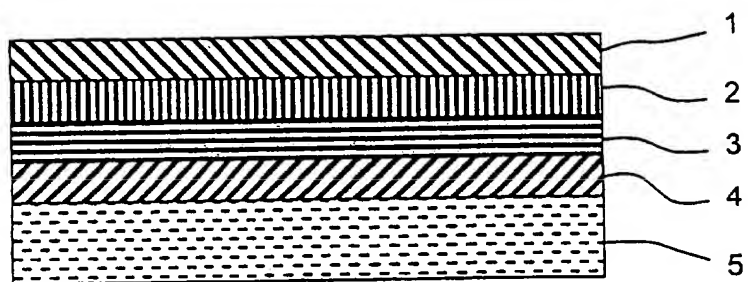


Figure 1

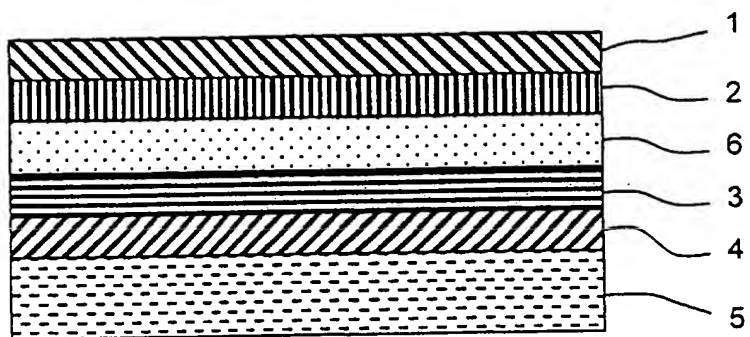


Figure 2

Hot Stamping Foils

Field of the Invention

- 5 The invention relates to hot stamping foils comprising liquid crystal material. The invention further relates to a method of preparing a hot stamping foil and to the use of hot stamping foils for decorative uses, information storage and security applications. The invention also relates to a security marking applied e.g. onto a document, object or
10 device by means of a hot stamping foil.

Brief Description of the Drawings

- 15 Figure 1 depicts a hot stamping foil according to prior art.
- Figure 2 depicts a hot stamping foil according to the present invention.

20 Background and Prior Art

- Hot stamping foils are known in prior art, where they are also named hot blocking foils, to provide e.g. images, signs, letters or patterns onto a substrate or an object like e.g. a car number plate. For
25 example WO 94/25295 discloses a hot blocking foil for the production of car number plates comprising a layer of decorative lacquer with luminescent pigments.

- 30 **Figure 1** schematically depicts a typical assembly of a hot stamping foil according to prior art, comprising a layer of hot melt adhesive 1, a reflective layer of e.g. metal 2, a layer of coloured lacquer 3 and a wax release layer 4, which are provided on a plastic film 5 as supporting layer.

- 35 To use the hot stamping foil a patterned hot metal stamp is placed onto the support 5 and the foil held with its hot melt adhesive side

against a substrate such as paper. Due to the patterned surface of the hot metal stamp some areas of the stamp are in contact with the hot stamping foil while other areas of the stamp are not. The heat from the stamp melts the adhesive 1 in the contact areas and makes
5 them adhere to the paper where the adhesive has melted. When pulling away the hot stamping foil only those parts that have been affected by the hot stamp will glue to the paper, while the other parts are pulled away leaving an image of the stamp on the paper. Thereby, e.g. images or patterns can be applied to objects or
10 substrates for decorative or identification purposes.

Another field of use for hot stamping foils are security markings, e.g. on banknotes or documents of value, to prevent counterfeiting them.

15

Summary of the Invention

It was an aim of the present invention to provide hot stamping foils that do not show the drawbacks of prior art as mentioned above.
20 Another aim of the present invention was to provide methods of manufacturing hot stamping foil that are especially suitable for mass production. Other aims of the present invention are immediately obvious to the expert from the following description.

25 The inventors have found that particularly striking colour effects can be achieved by providing a hot stamping foil according to the present invention comprising a layer of liquid crystal material. Depending on the orientation of the liquid crystal material different angle dependent colour effects can be realized. By means of the inventive hot
30 stamping foils it is possible to apply security markings e.g. to documents or objects in order to provide improved safety or against counterfeiting, since the characteristic viewing angle dependent colour effect of the liquid crystal layer cannot be duplicated e.g. by
35 copying the security marking.

One object of the invention is a hot stamping foil, characterized in that it comprises at least one layer of liquid crystal material.

5 Another object of the invention is a process of preparing an inventive hot stamping foil.

Another object of the invention is the use of an inventive hot stamping foil for decorative uses, optical information storage or security applications.

10 Another object of the invention is a security marking applied to a document or device by means of an inventive hot stamping foil.

15 Definition of Terms

In connection with liquid crystal layers and films as described in the present application, the following definitions of terms as used throughout this application are given.

20 The term 'film' as used in this application includes self-supporting, i.e. free-standing, films that show more or less pronounced mechanical stability and flexibility, as well as coatings or layers on a supporting substrate or between two substrates.

25 The term 'liquid crystal or mesogenic material' or 'liquid crystal or mesogenic compound' should denote materials or compounds comprising one or more rod-shaped, board-shaped or disk-shaped mesogenic groups, i.e. groups with the ability to induce liquid crystal phase behaviour. The compounds or materials comprising
30 mesogenic groups do not necessarily have to exhibit a liquid crystal phase themselves. It is also possible that they show liquid crystal phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are
35 polymerized.

For the sake of simplicity, the term 'liquid crystal material' is used hereinafter for both liquid crystal materials and mesogenic materials, and the term 'mesogen' is used for the mesogenic groups of the material.

5 The term 'planar structure' or 'planar orientation' means that the liquid crystal director, i.e. the preferred orientation direction of the main molecular axes of the mesogens in the liquid crystal material, is substantially parallel to the plane of the film or layer. This definition also includes films wherein the director is slightly tilted relative to the
10 film plane, with an average tilt angle throughout the film of up to 1 °, and which exhibit the same optical properties as a film wherein the director is exactly parallel, i.e. with zero tilt, to the film plane.

15 The terms 'tilted structure' or 'tilted orientation' means that the liquid crystal director of the film is tilted at an angle θ between 0 and 90 degrees relative to the film plane.

20 The term 'splayed structure' or 'splayed orientation' means a tilted orientation as defined above, wherein the tilt angle additionally varies monotonously in the range from 0 to 90 °, preferably from a minimum to a maximum value, in a direction perpendicular to the film plane.

25 The term 'low tilt structure' or 'low tilt orientation' means that the optical axis of the film is slightly tilted or splayed as described above, with the average tilt angle throughout the film being between 1 and 10 °.

The average tilt angle θ_{ave} is defined as follows

30
$$\theta_{ave} = \frac{\sum_{d'=0}^d \theta'(d')}{d}$$

wherein $\theta'(d')$ is the local tilt angle at the thickness d' within the film, and d is the total thickness of the film.

35 The tilt angle of a splayed film hereinafter is given as the average tilt angle θ_{ave} , unless stated otherwise.

5 The term 'homeotropic structure' or 'homeotropic orientation' means that the liquid crystal director of the film is substantially perpendicular to the film plane, i.e. substantially parallel to the film normal. This definition also includes films wherein the director is slightly tilted at an angle of up to 2 ° relative to the film normal, and which exhibit the same optical properties as a film wherein the director is exactly parallel, i.e. with no tilt, to the film normal.

10 For sake of simplicity, a film comprising liquid crystal material with a tilted, splayed, low tilted, planar and homeotropic orientation or structure is hereinafter being shortly referred to as 'tilted film', 'splayed film', 'low tilt film', 'planar film' and 'homeotropic film', respectively.

15

Detailed Description of the Invention

Preferred embodiments of the invention relate to hot stamping foils wherein

20

- the layer of liquid crystal material essentially consists of polymerized liquid crystal material,

- the reflective layer is a metal layer,

25

- the layer of liquid crystal material comprises polymerized and unpolymerized liquid crystal material,

- the polymerized liquid crystalline material is a linear or crosslinked liquid crystal side chain polymer,

- the liquid crystal material exhibits a planar orientation,

30

- the liquid crystal material exhibits a homeotropic orientation,

- the liquid crystal material exhibits a tilted orientation,

- the liquid crystal material additionally comprises at least one isotropic dye,

35

- the liquid crystal material additionally comprises at least one dichroic dye.

Figure 2 exemplarily depicts a hot stamping foil according to a preferred embodiment of the present invention, comprising a layer of hot melt adhesive 1, a reflective layer of e.g. metal 2, a liquid crystal layer 6, a layer of clear or coloured lacquer 3, and a wax release layer 4 on a support 5 like e.g. a PET film.

To use the inventive hot stamping foil a patterned hot metal stamp is placed onto the support 5 and the foil held with its hot melt adhesive layer 1 against a substrate, e.g. a sheet of paper or plastic. The areas of the adhesive layer 1 that are in direct contact with the hot stamp will melt and adhere to the substrate. At the same time, the areas of the wax release layer 4 that are in contact with the hot stamp will melt, allowing to release the support 5 from the wax layer 4 in these areas.

The hot stamp is then released from the hot stamping foil and the foil pulled away from the substrate. In the areas of the foil that have been affected by the hot stamp, the adhesive 1 will glue to the substrate, thus the hot stamping foil will be torn apart between the molten wax release layer 4 and the support 5, leaving the layers of molten adhesive 1, metal 2, liquid crystal material 6 and lacquer 3 on the substrate. In the other areas, the hot stamping foil will be released completely from the substrate, thus leaving an image of the stamp on the substrate.

The layer or film 6 of liquid crystal material that remains on the substrate is e.g. a clear, non-scattering thin film of planar aligned nematic or smectic liquid crystal material, and is underlaid by the metal layer 3, which consists for example of aluminium. When viewed under unpolarized light the liquid crystal film 6 is invisible.

If the liquid crystal film is irradiated with light passing through a first polarizer, and the viewer looks at the film in reflection through a second polarizer that is crossed with respect to the first polarizer, a bright birefringence colour is observed. This colour changes as the

substrate with the liquid crystal film is rotated relatively to the polarization directions of the two polarizers. Thus, by changing the angle of polarizers and/or the angle of the director of the liquid crystal film, different colour effects can be observed.

5

However, viewing of these liquid crystal films when incorporated in a hot stamping foil is best achieved using a single linear polarizer. The effect is observed by rotating the linear polarizer over the film whereby a colour will be seen according to the relative orientation of the polarizer with respect to the film. The actual colours observed will depend upon the thickness and birefringence of the liquid crystal film. These colours would be the same in transmission when viewed between two polarizers crossed at 90° to each other; complimentary colours would be seen if the polarizers are not crossed with respect to each other.

10
15

The liquid crystal layer 6 preferably comprises a linear or crosslinked liquid crystal polymer with macroscopically uniform orientation.

20

Brittle liquid crystal polymer films are preferred as these break more easily when releasing the hot stamping foil from the substrate or object to be decorated. Flexible films on the other hand are less preferred as they do not break easily, and therefore leave all the liquid crystal film on the substrate, which is however only glued to the substrate in the areas affected by the hot stamp.

25

Especially preferred are liquid crystal side chain polymers with rod-shaped mesogenic groups that are laterally attached via a spacer group to the polymer backbone, as described in US 5,190,689.

30

Further preferred are copolymers comprising both monomer units with laterally and terminally attached rod-shaped mesogenic groups.

35

Preferably the liquid crystal layer is prepared by coating a layer of polymerizable liquid crystal material onto a substrate, e.g. a plastic film, aligning the material into macroscopically uniform planar orientation, and polymerizing or crosslinking the material by

exposure to heat or actinic radiation. For example, a polymerizable liquid crystal material can be used comprising a photoinitiator, which is then cured by UV radiation. Suitable methods and materials for this technique are described in D.J.Broer et al., Makromol.Chem. 190, pp. 2255 ff. (1989). The polymerized liquid crystal film can then be released from the plastic film, one of its surfaces covered with a wax release layer and laminated onto a plastic film e.g. of PET, and the other surface covered with a metal film or layer.

It is also possible to coat or laminate the layer of polymerizable liquid crystal material directly onto the reflective layer which serves as a substrate.

Alternatively to the above method it is possible to coat or laminate a liquid crystal polymer, preferably a liquid crystal side chain polymer, onto a substrate, and align the polymer into uniform orientation. For this purpose, preferably low molecular weight polymers are used, as these align more easily. The polymer may be crosslinked after coating or lamination to increase its brittleness and thermal stability.

Preferably the liquid crystal layer has a planar orientation. The preparation of polymerized liquid crystal films with planar orientation is described in WO 98/04651, the entire disclosure of which is incorporated into this application by way of reference.

Another preferred embodiment relates to hot stamping foils wherein the liquid crystal layer has a tilted or splayed orientation.

By using a liquid crystal film with tilted orientation, more subtle colour effects can be realized. When viewing such a film along the director orientation direction and increasing the viewing angle starting from normal incidence, the colour disappears when the viewing angle is identical to the tilt angle. At other viewing angles no effect is seen.

The preparation of polymerized liquid crystal films with tilted or splayed orientation is described in US 5,619,352, WO 97/44409, WO

97/44702, WO 97/44703 and WO 98/12584, with the entire disclosure of these documents being incorporated into this application by way of reference.

5 It is also possible to use a multilayer liquid crystal film comprising two or more sublayers of polymerized liquid crystal material, with each sublayer having a tilted structure with constant tilt angle, wherein said tilt angle increases or decreases continuously from one sublayer to the next sublayer throughout the multilayer.

10

In a preferred embodiment of the invention, the liquid crystal film is a tilted or splayed film as described in WO 98/12584, or a film prepared in analogy to the methods disclosed therein.

15 Alternatively it is possible to use a liquid crystal film as described in WO 96/10770, which is prepared from a polymerizable liquid crystal material with a smectic A or smectic C phase and a nematic phase at higher temperatures. The polymerizable liquid crystal material is applied in its nematic phase onto a substrate that is e.g covered with
20 an alignment layer of obliquely deposited SiOx, and lowering the temperature into smectic C phase of the material. This leads to an increase of the tilt angle, as the material adopts its naturally tilted smectic C structure, which is then fixed by polymerization of the liquid crystal material. The above preparation method and possible
25 variations thereof are described in detail in WO 96/10770, the entire disclosure of which is incorporated into this application by way of reference.

30 It is also possible to use a liquid crystal layer with low tilt structure, comprising one or more layers of polymerized liquid crystal material with a slightly tilted structure. Such layers can be prepared by using a high pre-tilt on the substrate surface combined with a liquid crystal material which gives planar alignment at the air interface. Alternatively a liquid crystal material with an optimised tilt angle can be used.

35

Another preferred embodiment relates to hot stamping foils wherein the liquid crystal layer has a homeotropic orientation.

5 When using a liquid crystal film with homeotropic orientation, no effect is seen when viewing the film at normal incidence either between crossed polarizers or under unpolarized light. However, when the angle of incidence is increased the film looks progressively more white between crossed polarizers in reflected light, whereas the complementary colour is seen in transmission.

10 The preparation of polymerized liquid crystal films with homeotropic orientation is described in WO 98/00475, the entire disclosure of which is incorporated into this application by way of reference.

15 Changing the thickness of the liquid crystal film also leads to different colours, thin films giving first order white and yellows and thicker films giving reds and blues. By using thin films of a liquid crystal material with a high birefringence value, the thickness of the films can be reduced, compared e.g. to birefringent films of stretched
20 conventional polymers. This is a considerable advantage for practical applications, where often thin layers are desired.

The thickness of tilted and splayed liquid crystal films is preferably from 0.2 to 5 μm , in particular from 0.5 to 3 μm , very preferably from
25 1 to 2 μm . The thickness of homeotropic liquid crystal films is preferably from 1 to 10 μm , in particular from 2 to 7 μm , very preferably from 3 to 6 μm .

30 If the hot stamping foil as exemplarily depicted in **Figure 2** is applied onto a transparent substrate, e.g. a transparent plastic sheet, in the way as described above, the image that is left on the substrate after releasing the hot stamping foil can be viewed both in transmission and in reflection, depending on the transparency of the reflective layer 2. When the image is illuminated with a backlight of very high
35 luminance, even reflective layers of thin metal films 2 like e.g. aluminium show a certain degree of transparency.

Thus, another preferred embodiment relates to hot stamping foils wherein the type and thickness of reflective layer are selected such that it is transmissive under strong backlight conditions.

5

When viewing the liquid crystal layer under polarized light in transmission instead of reflection, the complementary colours are seen. Thus e.g. a yellow film in reflection is blue in transmission.

10

The reflective layer has preferably a thickness from 0.1 to 100 nm, in particular from 1 to 50 nm, very preferably from 1 to 10 nm.

15

For the reflective layer in principle any reflective material can be used. The reflective layer is preferably a metal film of e.g. Al, Cu, Ni, Ag, Au, Cr or alloys like e.g. Pt-Rh or Ni-Cr, especially preferably of Al. Such metal layers can be prepared e.g. by vacuum deposition or sputtering.

20

Further preferred are reflective layers comprising one or more metal flakes of e.g. aluminium, gold or titan, or metal oxide flakes of e.g. TiO_2 . Especially preferred are reflective layers comprising one or more pearlescent pigment flakes comprising a substrate of e.g. mica, SiO_2 , Al_2O_3 , TiO_2 or glass that is coated with one or more layers of e.g. titanium dioxide, iron oxide, titanium iron oxide or chrome oxide or combinations thereof, or flakes comprising combinations of metal and metal oxide. Further preferred are e.g. metal flakes of e.g. aluminium coated with layers of iron oxide layers and/or silicon dioxide. Particularly suitable pearlescent pigments are e.g. the commercially available Iriodin or Xirallic (from Merck KGaA, Darmstadt, Germany), or Paliochrome (from BASF AG, Ludwigshafen, Germany). Further suitable pigments are optically variable pigments like e.g. Flex pigments, comprising a substrate of e.g. aluminium that is sandwiched between layers of e.g. MgF and coated with top layers of e.g. chrome or molybdenum.

25

30

35

For use as reflective layer the above pigments are preferably dispersed in a light transmissive binder.

5 According to another preferred embodiment the reflective layer is a holographic layer with a structured surface, e.g. a holographic effect plastic substrate, or a layer of reflective holographic pigments. Light reflected by higher regions of the structured surface will interfere with light reflected by lower regions of the structured surface, thereby forming a holographic image.

10 In case a metal layer is used as reflective layer, this can be applied by evaporating e.g. aluminium or another suitable metal onto the liquid crystal layer, followed by coating an adhesive layer on top of the reflective layer.

15 The lacquer layer is typically a polyacrylate, polyurethane or other solvent cast polymer.

20 The lacquer can be clear or coloured. It is also possible to use one or more layers of coloured lacquers covered by a clear lacquer layer, also called 'clear coat', on the side facing the wax release layer.

The lacquer may comprise dyes or pigments, like e.g. solvent dyes such as waxoline green and waxoline red.

25 It is also possible to incorporate isotropic dyes into the liquid crystal material, giving a film that is coloured in normal light but shows the above birefringence effects in polarized light.

30 Furthermore, it is possible to incorporate one or more dichroic dyes into the liquid crystal material, giving a film that is coloured in normal light but acts as a linear polarizer in polarized light, thus changing from a bright to dark appearance when rotated in polarized light. In this case a second polarizer is not needed as the dichroic dye allows the effects of the polarized light to be seen.

35

Thus, according to another preferred embodiment the liquid crystal layer of the inventive hot stamping foil comprises at least one dye, very preferably at least one dichroic dye.

- 5 Suitable dyes are e.g. solvent dyes such as waxoline green and waxoline red. Suitable dichroic dyes are e.g. D35, a magenta dye, or D16, a blue dye, both commercially available from Merck Ltd. UK.

- 10 The wax release layer comprises e.g. abherents such as hydrocarbon or natural ester waxes like Carnauba wax, synthetical waxes, petroleum waxes like paraffin wax or blends with polyethylen, waxy amides like ethylene bis(stearamide), esters of high molecular weight aliphatic alcohols and fatty acids like e.g. stearic acid, stearate salts of e.g. zinc, barium, cadmium, aluminium
15 or lithium.

- 20 The adhesive layer can comprise hot melt adhesives known to the expert from the state of the art, e.g. hydrocarbon resins such as ethylene - vinyl acetate (EVA), ethylene - methyl acrylate (EMA) and low molecular weight polyethylene, styrene block copolymers (S) with isoprene (I) and/or butadiene (B), like SIS, SBS or combinations thereof, or epoxides.

- 25 The inventive hot stamping foils can be used for direct application onto substrates like e.g. paper, plastic films or sheets, onto objects or devices for decorative uses or for security uses, e.g. to authenticate and prevent counterfeiting of banknotes, documents of value, for identification of hidden images, informations or patterns. They can be applied to consumer products or household objects, car bodies, foils,
30 packing materials, clothes or woven fabric, or applied as security markings or threads on banknotes, documents of value, credit cards or ID cards or passports.

- 35 The inventive hot stamping foils are especially suitable for security uses, as the polarized light effect is simple to see using cheap and available detection equipment like standard linear polarizers, is not

visible in normal light, can have at least two different modes of operation, i.e. in transmission or reflection, and can be extended using isotropic and/or dichroic dyes.

5 Preferred embodiments of the invention as described above relate to hot stamping foils wherein the liquid crystal layer is essentially consisting of a linear or crosslinked polymerized liquid crystal (LC) material with macroscopically uniform orientation.

10 The polymerized LC layer is preferably obtained by coating a layer of a polymerizable LC material onto a substrate or between two substrates, aligning the material into the desired orientation, and polymerizing the material by exposure to heat or actinic radiation.

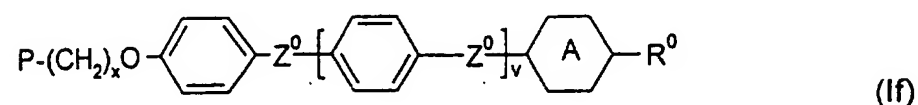
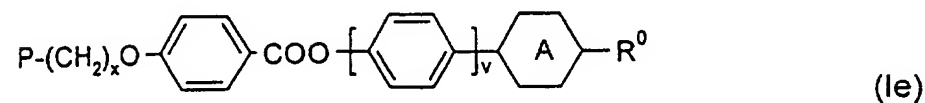
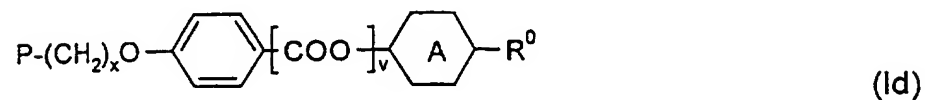
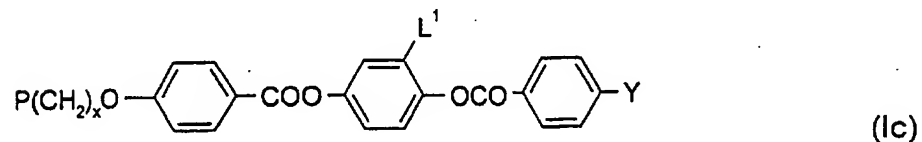
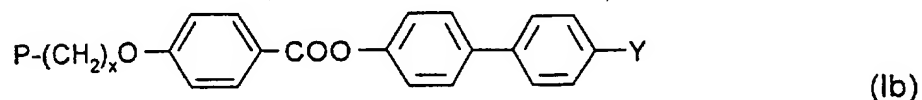
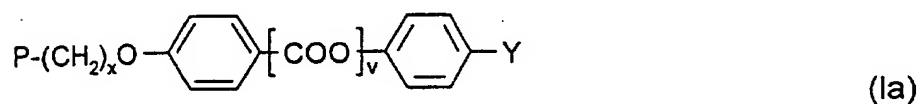
15 Preferably a polymerizable LC material is used that consists essentially of achiral polymerizable mesogenic compounds. Very preferably a polymerizable LC material is used that comprises at least one polymerizable mesogen having one polymerizable functional group and at least one polymerizable mesogen having two
20 or more polymerizable functional groups.

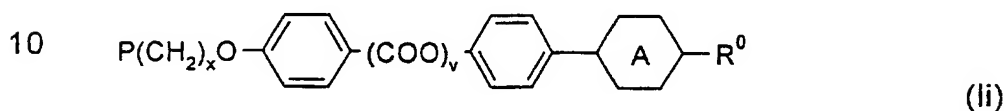
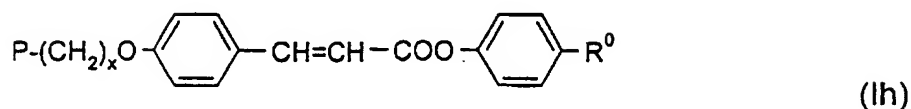
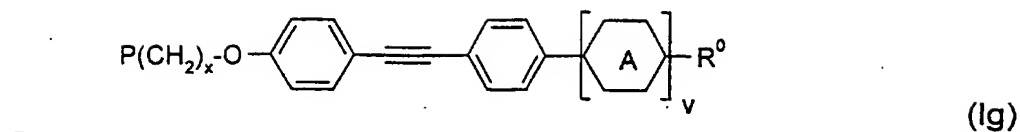
In another preferred embodiment the polymerizable LC material comprises polymerizable mesogenic compounds having two or more polymerizable functional groups (di- or multireactive or di- or
25 multifunctional compounds). Upon polymerization of such a mixture a three-dimensional polymer network is formed. A film made of such a network is self-supporting and shows a high mechanical and thermal stability and a low temperature dependence of its physical and optical properties.

30 By varying the concentration of the multifunctional mesogenic or non mesogenic compounds the crosslink density of the polymer film and thereby its physical and chemical properties such as the brittleness and the glass transition temperature, can be tuned easily. This is
35 also important for the optical properties, the thermal and mechanical stability or the solvent resistance of the polymerized film.

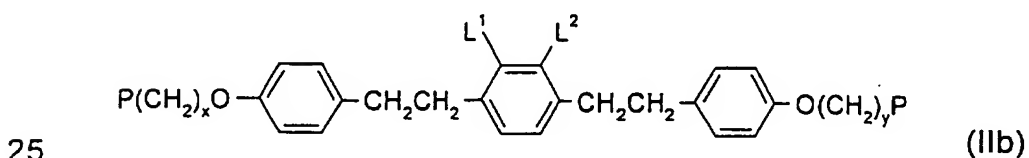
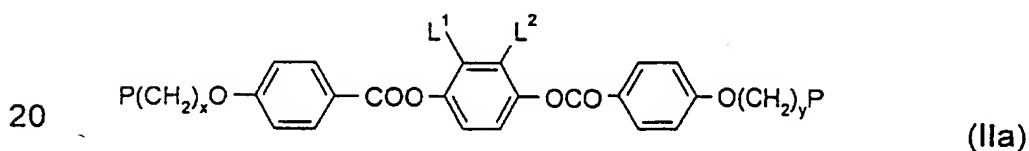
The polymerizable mesogenic mono-, di- or multireactive compounds can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Typical examples are described for example in WO 93/22397; EP 0 261 712; DE 19504224; DE 4408171 and DE 4405316. The compounds disclosed in these documents, however, are to be regarded merely as examples that do not limit the scope of this invention.

Examples representing especially useful monoreactive polymerizable mesogenic compounds are shown in the following list of compounds, which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention:





15 Examples of useful direactive polymerizable mesogenic compounds are shown in the following list of compounds, which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention



30 In the above formulae, P is a polymerizable group, preferably an acryl, methacryl, vinyl, vinyloxy, propenyl ether, epoxy or styryl group, x and y are each independently 1 to 12, A is 1,4-phenylene that is optionally mono- di or trisubstituted by L¹ or 1,4-cyclohexylene, v is 0 or 1, Z⁰ is -COO-, -OCO-, -CH₂CH₂- or a single bond, Y is a polar group, R⁰ is an unpolar alkyl or alkoxy group, and L¹ and L² are each independently H, F, Cl, CN or an optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkoxy carbonyl or
35 alkoxy carbonyloxy group with 1 to 7 C atoms.

The term 'polar group' in this connection means a group selected from F, Cl, CN, NO₂, OH, OCH₃, OCN, SCN, an optionally fluorinated carbonyl or carboxyl group with up to 4 C atoms or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms.

5

The term 'unpolar group' means an alkyl group with 1 or more, preferably 1 to 12 C atoms or an alkoxy group with 2 or more, preferably 2 to 12 C atoms.

10

The polymerizable LC material is coated onto substrate, aligned into a uniform orientation and polymerized, as described e.g. in WO 98/12584, thereby permanently fixing the orientation of the polymerizable mesogenic material.

15

As a substrate for example a glass or quartz sheet or a plastic film or sheet can be used. It is also possible to put a second substrate on top of the coated mixture prior to and/or during and/or after polymerization. The substrates can be removed after polymerization or not. When using two substrates in case of curing by actinic

20

radiation, at least one substrate has to be transmissive for the actinic radiation used for the polymerization. Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerized film after polymerization, preferably isotropic substrates are used.

25

Preferably at least one substrate is a plastic substrate such as for example a film of polyester such as polyethyleneterephthalate (PET), of polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC), especially preferably a PET film or a TAC film. As a

30

birefringent substrate for example an uniaxially stretched plastic film can be used. For example PET films are commercially available from ICI Corp. under the trade name Melinex.

35

The polymerizable LC material can also be dissolved in a solvent, preferably in an organic solvent. The solution is then coated onto the substrate, for example by spin-coating or other known techniques,

and the solvent is evaporated off before polymerization. In most cases it is suitable to heat the mixture in order to facilitate the evaporation of the solvent.

- 5 Macroscopically uniform planar orientation of polymerizable LC material can be achieved for example by shearing the material, e.g. by means of a doctor blade.

- 10 Planar alignment can be achieved e.g. by means of an alignment layer, for example a layer of rubbed polyimide or other rubbed polymer layers, like e.g. PVA, or sputtered SiO_x , that is applied on top of the substrate.

- 15 Planar alignment of the polymerizable LC material can also be achieved by directly rubbing the substrate, i.e. without applying an additional alignment layer. This is a considerable advantage as it allows a significant reduction of the production costs of the LC polymer film. In this way a low tilt angle can easily be achieved.

- 20 For example rubbing can be achieved by means of a rubbing cloth, such as a velvet cloth, or with a flat bar coated with a rubbing cloth. In a preferred embodiment of the present invention rubbing is achieved by means of at least one rubbing roller, like e.g. a fast spinning roller that is brushing across the substrate, or by putting the substrate between at least two rollers, wherein in each case at least one of the rollers is optionally covered with a rubbing cloth. In another preferred embodiment of the present invention rubbing is achieved by wrapping the substrate at least partially at a defined angle around a roller that is preferably coated with a rubbing cloth.

- 30 The polymerizable LC material may also comprise one or more surfactants to improve planar alignment. Suitable surfactants are described for example in J. Cognard, Mol.Cryst.Liq.Cryst. 78, Supplement 1, 1-77 (1981). Particularly preferred are non-ionic surfactants, such as the commercially available fluorocarbon surfactants Fluorad FC-171 (from 3M Co.), or Zonyl FSN (from
- 35

DuPont). Preferably the polymerizable mixture comprises 0.01 to 5 %, in particular 0.1 to 3 %, very preferably 0.2 to 2 % by weight of surfactants.

5 Homeotropic alignment can be achieved e.g. by means of an alignment layer coated on top of the substrate. Suitable aligning agents used on glass substrates are for example alkyltrichlorosilane, chrome complexes or lecithine, whereas for a plastic substrate thin
10 layers of lecithine, silica or high tilt polyimide orientation films as aligning agents may be used. In a preferred embodiment of the invention a silica coated plastic film is used as a substrate. Furthermore, homeotropic alignment can be achieved by using aluminium oxide films as described in GB 2,324,382.

15 Further suitable methods to achieve planar or homeotropic alignment are described for example in J. Cognard, Mol.Cryst.Liq.Cryst. 78, Supplement 1, 1-77 (1981).

20 Tilted alignment can be achieved by methods as described in US 5,619,352, WO 97/44409, WO 97/44702, WO 97/44703 or WO 98/12584, the entire disclosure of which is incorporated into this application by way of reference.

25 Furthermore, alignment can be achieved by using alignment layers obtained by photopolymerization of e.g. polymethoxycinnamate or coumarin derivatives under linear polarized UV light.

30 The orientation of the polymerizable LC material depends, inter alia, on the film thickness, the type of substrate material, and the composition of the polymerizable LC material. It is therefore possible, by changing these parameters, to control the orientation, in particular specific parameters such as the tilt angle and its degree of variation.

35 Thus, for the preparation of a film of polymerized LC material with tilted structure, it is possible to adjust the alignment profile in the direction perpendicular to the film plane by appropriate selection of

the ratio of monoreactive mesogenic compounds, i.e. compounds with one polymerizable group, and direactive mesogenic compounds, i.e. compounds with two polymerizable groups.

5 To achieve a film with splayed structure, i.e. a variation of the tilt angle throughout the thickness of the film, preferably the ratio of mono- to direactive mesogenic compounds should be in the range of 6:1 to 1:2, preferably 3:1 to 1:1, especially preferably about 3:2.

10 Another effective means to adjust the desired splay geometry is to use a defined amount of dielectrically polar polymerizable mesogenic compounds in the polymerizable mesogenic material. These polar compounds can be either monoreactive or direactive. They can be
15 dielectrically positive or negative. Most preferred are dielectrically positive and monoreactive mesogenic compounds.

The amount of the polar compounds in the polymerizable LC material is preferably 1 to 80 %, especially 3 to 60 %, in particular 5 to 40 %
20 by weight of the total mixture.

Polar mesogenic compound in this connection means a compound with one or more polar groups as defined above. Especially preferred are monoreactive polar compounds selected from formulae Ia to Ic
25 given above.

Furthermore, these polar compounds preferably exhibit a high absolute value of the dielectric anisotropy $\Delta\epsilon$, which is typically higher than 1.5. Thus, dielectrically positive compounds preferably exhibit
30 $\Delta\epsilon > 1.5$ and dielectrically negative polar compounds preferably exhibit $\Delta\epsilon < -1.5$. Very preferred are dielectrically positive polar compounds with $\Delta\epsilon > 3$, in particular with $\Delta\epsilon > 5$.

Polymerization of the polymerizable LC material takes place by exposing it to heat or actinic radiation. Actinic radiation means
35 irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles,

such as ions or electrons. Preferably polymerization is carried out by UV irradiation.

5 As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

10 The polymerization is carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerizing by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerization reaction.

15 When curing polymerizable mesogens with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerizable mesogens vinyl and epoxide groups, preferably a cationic photoinitiator is used.

20 It is also possible to use a polymerization initiator that decomposes when heated to produce free radicals or ions that start the polymerization.

25 As a photoinitiator for radical polymerization for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerization the commercially available UVI 6974 (Union Carbide) can be used.

30 The polymerizable (C)LC material preferably comprises 0.01 to 10 %, very preferably 0.05 to 5 %, in particular 0.1 to 3 % of a polymerization initiator. UV photoinitiators are preferred, in particular radicalic UV photoinitiators.

35 The curing time is depending, inter alia, on the reactivity of the polymerizable mesogenic material, the thickness of the coated layer,

the type of polymerization initiator and the power of the UV lamp. The curing time according to the invention is preferably not longer than 10 minutes, particularly preferably not longer than 5 minutes and very particularly preferably shorter than 2 minutes. For mass
5 production short curing times of 3 minutes or less, very preferably of 1 minute or less, in particular of 30 seconds or less, are preferred.

In addition to polymerization initiators the polymerizable LC material may also comprise one or more other suitable components such as, for
10 example, catalysts, stabilizers, chain-transfer agents, co-reacting monomers or surface-active compounds. In particular the addition of stabilizers is preferred in order to prevent undesired spontaneous polymerization of the polymerizable material for example during storage.

15 As stabilizers in principal all compounds can be used that are known to the skilled in the art for this purpose. These compounds are commercially available in a broad variety. Typical examples for stabilizers are 4-ethoxyphenol or butylated hydroxytoluene (BHT).

20 Other additives, like e.g. chain transfer agents, can also be added to the polymerizable LC material in order to modify the physical properties of the resulting polymer film. When adding a chain transfer agent, such as monofunctional thiol compounds like e.g. dodecane thiol or multifunctional thiol compounds like e.g.
25 trimethylpropane tri(3-mercaptopropionate), to the polymerizable material, the length of the free polymer chains and/or the length of the polymer chains between two crosslinks in the inventive polymer film can be controlled. When the amount of the chain transfer agent is increased, the polymer chain length in the obtained polymer film is
30 decreasing.

It is also possible, in order to increase crosslinking of the polymers, to add up to 20% of a non mesogenic compound with two or more polymerizable functional groups to the polymerizable LC material
35 alternatively or in addition to the di- or multifunctional polymerizable mesogenic compounds to increase crosslinking of the polymer.

Typical examples for difunctional non mesogenic monomers are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more
5 than two polymerizable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

In another preferred embodiment the mixture of polymerizable material comprises up to 70%, preferably 3 to 50 % of a non
10 mesogenic compound with one polymerizable functional group. Typical examples for monofunctional non mesogenic monomers are alkylacrylates or alkylmethacrylates.

It is also possible to add, for example, a quantity of up to 20% by
15 weight of a non polymerizable liquid-crystalline compound to adapt the optical properties of the resulting polymer film.

In some cases it is of advantage to apply a second substrate to aid alignment and exclude oxygen that may inhibit the polymerization.
20 Alternatively the curing can be carried out under an atmosphere of inert gas. However, curing in air is also possible using suitable photoinitiators and high UV lamp power. When using a cationic photoinitiator oxygen exclusion most often is not needed, but water should be excluded. In a preferred embodiment of the invention the
25 polymerization of the polymerizable mesogenic material is carried out under an atmosphere of inert gas, preferably under a nitrogen atmosphere.

To obtain a polymer film with the desired molecular orientation the
30 polymerization has to be carried out in the liquid crystal phase of the polymerizable LC material. Therefore, preferably polymerizable mesogenic compounds or mixtures with low melting points and broad liquid crystal phase ranges are used. The use of such materials allows to reduce the polymerization temperature, which
35 makes the polymerization process easier and is a considerable advantage especially for mass production.

5 The selection of suitable polymerization temperatures depends mainly on the clearing point of the polymerizable material and inter alia on the softening point of the substrate. Preferably the polymerization temperature is at least 30 degrees below the clearing temperature of the polymerizable mesogenic mixture.

10 Polymerization temperatures below 120 °C are preferred. Especially preferred are temperatures below 90 °C, in particular temperatures of 60 °C or less.

15 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

20 In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight.

Example 1

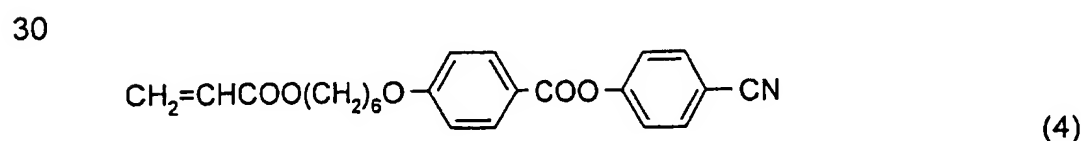
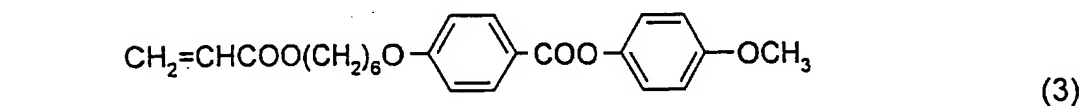
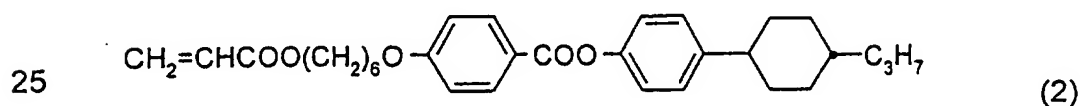
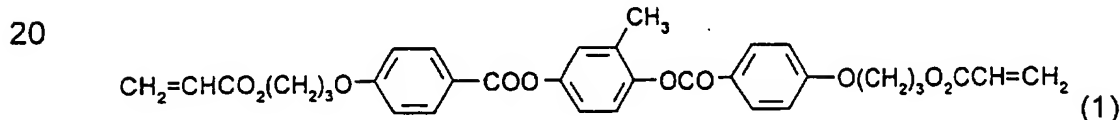
25 Polyvinyl alcohol (PVA) dissolved in water (1 %) is coated onto a polyurethane lacquer that has been coated onto a wax in turn coated onto a thin PET substrate. Drying in a warm oven at 40 °C evaporates the water. The PVA is then unidirectionally rubbed using a velvet cloth, such that when a solution of reactive liquid crystals (Mixture 1) as described below is coated onto the PVA using a bar
30 coating technique, a film of about 1 micron thickness is left after evaporation of the solvent. This film is then cured by exposure to UV light (10 mW/cm² at 365 nm) in air atmosphere to give a hard film having good adhesion to the PVA layer. Aluminium is then
35 evaporated onto the polymerized liquid crystal film and then hot melt adhesive is coated from solution onto the aluminium layer.

On heating the film from the PET side onto paper, e.g. by means of a hot stamp, the film is released onto the paper. When viewed with a polarizer with the optic axis of the liquid crystal film at 45 ° to the polarizer fast direction a bright colour is seen only where the liquid crystal film is deposited, whereas the colour is not visible without the use of polarized light. The orientation of the nematic director in the liquid crystal film is slightly tilted relative to the plane of the film, thus giving a slightly non-symmetric colour change.

10 Preparation of Mixture 1

The following reactive liquid crystal mixture is formulated

compound (1)	31 %
compound (2)	22 %
compound (3)	12 %
compound (4)	29 %
Irgacure 907	1.0 %



35 Compounds (1), (3) and (4) can be prepared according to or in analogy to the methods described in D.J.Broer et al., Makromol.Chem. **190**, 3201-3215 (1989). Compound (2) and its

preparation are described in GB 2,280,445. Irgacure 907 is a commercially available photoinitiator (from Ciba Geigy).

5 The above reactive liquid crystal mixture has a nematic phase with a clearing point of 73 °C.

10 The above reactive liquid crystal mixture is added to a mixture of toluene (2.3 parts) and cyclohexanone (1 part) in the ratio solvent 75 % and reactive liquid crystals 25 % to give Mixture 1.

15 The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

20 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

25

30

35

Claims

1. A hot stamping foil, comprising at least one layer of liquid crystalline material.
5
2. A hot stamping foil as claimed in claim 1, additionally comprising at least one hot melt adhesive layer, at least one reflective layer and at least one wax release layer, provided on a supporting substrate.
10
3. A hot stamping foil as claimed in claim 1 or claim 2, wherein the reflective layer is a metal layer.
4. A hot stamping foil as claimed in any of the preceding claims,
15 wherein the layer of liquid crystalline material essentially consists of polymerized liquid crystalline material.
5. A hot stamping foil as claimed in any of claims 1 to 3, wherein the layer of liquid crystalline material comprises polymerized and
20 unpolymerized liquid crystalline material.
6. A hot stamping foil as claimed in any of the preceding claims, wherein said polymerized liquid crystalline material is a linear or crosslinked liquid crystal side chain polymer.
25
7. A hot stamping foil as claimed in any of the preceding claims, wherein according to at least one of claims 1 to 6, the liquid crystalline material exhibits a planar orientation.
- 30 8. A hot stamping foil as claimed in any of claims 1 to 6, wherein the liquid crystalline material exhibits a tilted orientation.

9. A hot stamping foil as claimed in any of claims 1 to 6, wherein the liquid crystalline material exhibits a homeotropic orientation.
- 5 10. A hot stamping foil as claimed in any of the preceding claims, wherein the liquid crystalline material additionally comprises at least one isotropic or dichroic dye.
11. A hot stamping foil substantially as hereinbefore described in the foregoing example.
- 10 12. A hot stamping foil substantially as hereinbefore described with reference to Figure 2.
13. Use of a hot stamping foil as claimed in any of the preceding claims,
15 for decorative uses, optical information storage or security applications.
14. As security marking applied to a document, object or device by means of a hot stamping foil as claimed in any of claims 1 to 12.



Application No: GB 0029163.3
Claims searched: 1-14

Examiner: Keith Kennett
Date of search: 12 February 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): B6J (JE, JF2, JF9)

Int Cl (Ed.7): B41M 1/24, 3/12, 3/14; B44C 1/17

Other: Online: EPODOC, WPI, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0911758 A2 (NHK) see column 5 line 55 to column 6 line 26	1-4,13,14

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.